

35. (New) The creep resistant zirconium alloy of claim 30, wherein the microstructure has a acicular structure comprising a lath spacing within the range from about 0.5 μ m to about 3.0 μ m.

REMARKS

Applicant thanks the Examiner for the attention accorded the present Application in the July 19, 2002 Office Action, in which claims 1-17 were pending. In that Action, claims 2 and 3 were rejected under 35 U.S.C. § 112, second paragraph as being indefinite; and claims 1-7 were rejected under 35 U.S.C. § 102(b) as being anticipated by Inagaki.

By the foregoing amendments, claims 2, 3, 6 and 7 have been amended to more clearly specify the present invention. Additionally, new claims 18-35 have been added. No new matter has been added, and the amendments and new claims are fully supported throughout the specification, as more fully described below.

Claims 1-7 and 18-35 are now currently pending in this Application. Based on the above amendments, Applicants respectfully submit that the rejections to claims 1-7 have been overcome. Reconsideration of this Application is respectfully requested in view of the foregoing amendments and the following remarks.

35 USC § 112, second paragraph rejections

Claims 2 and 3 stand rejected under 35 U.S.C. § 112, second paragraph as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. Claims 2 and 3 have been amended to remove the term "small." Additionally, claim 3 has been amended to correct the antecedent basis error noted by the Examiner. Finally, other minor errors in claims 2 and 3 have been corrected. Accordingly, Applicant respectfully requests that the Examiner withdraw this rejection and allow claims 2 and 3.

35 U.S.C. § 102 rejections

Claims 1-7 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Inagaki et al. The Examiner stated that “Inagaki et al. do not expressly teach that the α -phase of the zirconium is coarse-grained lath α microstructure ... [but] the method of forming the alloy taught by Inagaki et al. is substantially identical to the disclosed process, therefore, one of ordinary skill in the art would have expected that the products taught by ... [Inagaki] would inherently have the same coarse grained lath α microstructure as claimed [by Applicant].¹ Applicants respectfully disagree with the Examiner’s conclusion and submit that the present invention is not anticipated, nor even suggested, by Inagaki.

As presently claimed in Applicant’s independent claim 1, Applicant’s invention comprises “[a] creep resistant zirconium alloy comprising a coarse grained lath alpha microstructure.”² Applicant’s invention is formed by beta heat treating a zirconium alloy, fast quenching the alloy, cold working the alloy, and then annealing the alloy to effect partial recrystallization of the microstructure of the alloy. Applicant’s invention only cold works and anneals the alloy once. In fact, Applicant’s specification states that “[f]urther cold work would promote full recrystallization during the subsequent annealing step.”³ Furthermore, Applicant’s specification states that “[f]ull recrystallization would destroy the lath structure, and is undesirable.”⁴

In contrast, Inagaki does not disclose an alloy formed by performing cold working and annealing only one time each. Inagaki’s alloy is formed by, among other things, “*repetitional* treating cycles each comprising a cold plastic working and annealing.”⁵ All the examples in Inagaki disclose repeating the cold working and annealing steps *three* times each. As such, Inagaki’s alloy would not inherently have the same coarse grained lath alpha microstructure as claimed by Applicant. Therefore, Inagaki does not anticipate, nor even suggest, a creep resistant zirconium alloy comprising a coarse

¹ Office Action, ¶ 7.

² Applicant’s spec., independent claim 1.

³ Applicant’s spec., p. 8, lines 7-8.

⁴ Applicant’s spec., p. 6, lines 21-22.

⁵ Inagaki, independent claims 1, 3, 5 and 7 (emphasis added).

grained lath alpha microstructure, as recited in independent claim 1 of Applicant's invention.

As claims 2-7 depend from claim 1, the discussion above applies to these claims as well. Further, these claims each include separate novel features. Thus, Applicant respectfully requests allowance of pending claims 1-7.

New claims added

Applicants have also added new claims 18-35 to further define the present invention. No new matter has been added and these claims are fully supported by Applicants' specification at pages 6-8, and in original claims 1-7 and 10-13, among other places. Therefore, allowance of claims 18-35 is respectfully requested.

CONCLUSION

Applicant respectfully submits that the amendments to the claims successfully traverse the rejections given by the Examiner in the Office Action. For the above reasons, it is respectfully submitted that the claims now pending patentably distinguish the present invention from the cited references. Allowance of pending claims 1-7 and 18-35 is therefore respectfully requested.

As this reply is being timely filed within the 3 month time period, Applicant believes that the only fee due for this response is for the filing of additional claims (15 new claims in excess of twenty at \$18 each and 2 new independent claims in excess of three at \$84 each). Payment in the amount of \$438 is enclosed for these additional claims. If this amount is incorrect, the Commissioner is authorized to charge any additional fees that may be due, or credit any overpayment, to Deposit Account Number 04-1448.

Should the Examiner have any questions, or determine that any further action is necessary to place this Application into better form for allowance, the Examiner is encouraged to telephone the undersigned representative at the number listed below.

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PATENT

Respectfully submitted,

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Tracey R. Loughlin
Attorney for Applicant
Registration No. 51,969

Dougherty, Clements & Hofer
6230 Fairview Road, Suite 400
Charlotte, NC 28210
704-366-6642 Telephone
704-366-9744 Facsimile

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

Amendments in the Specification:

In accordance with 37 C.F.R. § 1.121(b), the following replacement paragraphs show all of the changes made by the foregoing amendments relative to the previous versions of the paragraphs. Material added is shown underlined, material deleted is shown in [brackets].

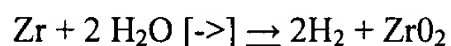
Please amend the second full paragraph on page 1 as follows:

Nuclear reactors utilize water as a coolant for the reactor and the produced steam as a source of energy to power steam turbines to thereby provide electrical energy. Nuclear reactors typically have their nuclear fissionable material contained in sealed cladding tubes, generally of a zirconium alloy, for isolation of the nuclear fuel from the water and/or steam. Zirconium and its alloys are widely used as nuclear fuel cladding since they advantageously possess low neutron absorption cross-sections, and at temperatures below about 398°C (the approximate core temperature of an operating nuclear reactor), are non-reactive and importantly possess high corrosion resistance relative to other metal alloys in the presence of de-mineralized water or steam. Two widely used zirconium alloys ([]Zircalloys[]) are []Zircaloy-2[] and []Zircaloy-4[]. Zircaloy-2, a Zr-Sn-Ni-Fe-Cr alloy, is generally comprised (by weight) of approximately 1.2-1.7% tin, 0.13-0.20% iron, 0.06-0.15% chromium and 0.05-0.08% nickel. Zircaloy-4 has essentially no nickel, and about 0.2% iron, but is otherwise substantially similar to Zircaloy-2. Zircaloy-2 has enjoyed widespread use and continues to be used at present in nuclear reactors. Zircaloy-4 was developed as an improvement to Zircaloy-2 to reduce problems with hydriding, which causes Zircaloy-2 to become brittle when cooled to ambient temperatures (ie. when the reactor is shut down) after absorbing hydrogen at higher temperatures.

Please amend the last paragraph beginning on page 1 as follows:

Zirconium alloys are among the best corrosion resistant materials when exposed to steam at reactor operating temperatures (less than 398°C, typically 290°C) in the absence of radiation from nuclear fission reactors. The corrosion rate in the absence of neutron bombardment is very low and the corrosion product is a uniform, black [ZrO₂ oxide] film/layer of ZrO₂ which forms on the exterior surfaces of Zircaloy that are exposed to high temperature steam (uniform corrosion). The black oxide layer of ZrO₂ usually contains a small (non-stoichiometric) excess of zirconium, and as such, it contains excess electrons giving it a black or grey color [colour]. It is also highly adherent to zirconium or Zircaloy surfaces that are exposed to steam.

Please amend the equation on page 2 as follows:



Please amend the second full paragraph on page 2 as follows:

Because gas permeability is typically limited in nuclear fuel rods, a hydrogen rich atmosphere, with a very low H₂O partial pressure, is generated inside the cladding, often far from the initial perforation, especially if crack growth is significant. The pressure in the hydrogen rich atmosphere is believed to be approximately 1000 psi, which is the pressure experienced inside the cladding near the perforation. Under these conditions, Zircaloy-2 cladding becomes susceptible to hydrogen embrittlement followed by failure by brittle fracture. It is, therefore, desirable to improve the resistance of Zircaloy-2 cladding to cracking, while retaining its resistance to fast fracture.

Please amend the last paragraph beginning on page 3 as follows:

It is observed that a zirconium alloy having a certain microstructural configuration and increased resistance to creep, has increased resistance to hydrogen gas cracking. In this regard, experimental results suggest that hydrogen gas fracture of the zirconium alloy is controlled by the rate of creep at the crack tip in the zirconium alloy.

Accordingly, the applicants have discovered a zirconium alloy of a particular microstructure which has increased resistance to creep, and which results in a zirconium alloy with increased resistance to hydrogen cracking. The applicants propose use of such alloy in nuclear fuel cladding due to such [alloy's] alloy's increased resistance to hydrogen cracking, which is problematic with existing zirconium and zirconium alloy fuel cladding.

Please amend the first full paragraph on page 4 as follows:

Accordingly, in a further aspect, the invention comprises a fuel cladding for use in a nuclear reactor having a microstructure in one or more of the embodiments disclosed above. More particularly, in a broad aspect of such [embodiment] embodiments of the invention, [then] the invention comprises a fuel cladding for use in a nuclear reactor, for cladding nuclear fuel, comprising:

a tube member; and

said tube member comprised of a zirconium alloy, said alloy having a coarse grained lath alpha microstructure.

Please amend the first full paragraph on page 6 as follows:

[Superior] A superior creep resistant zirconium alloy is provided for use in nuclear fuel cladding. The creep resistant zirconium alloy is a coarse grained lath alpha zirconium alloy microstructure. "Coarse grained" refers to the size of the grain boundary, and encompasses grains with a grain size greater than 0.15 μ m.

Please amend the last paragraph beginning on page 6 as follows:

In one embodiment, the microstructure is a lath or acicular structure and includes a lath (or interlamellar boundary) spacing of 0.5 to 3.0 μ m. Without wishing to be bound by theory, it is believed that the lath spacing provides significant obstacles to dislocations

during high strain creep. The lath spacing in the structure [create] creates an effective grain size much smaller than the apparent conventional grain size.

Please amend the first full paragraph on page 7 as follows:

Referring to Figures 1A and 1B, in one embodiment, an annular layer 12 of the above-described creep resistant zirconium alloy can be provided near the inside diameter 14 of fuel cladding 10, while retaining fast fracture resistant and corrosion resistant Zircaloy-2 on the outer portion 16 of the cladding. An annular layer 12 of such creep resistant zirconium alloy provided between a zirconium barrier layer 18 and the Zircaloy-2 cladding 16 of either conventional barrier fuel cladding or [Triclad□] TricladTM fuel cladding would help prevent hydrogen gas cracking from inside the cladding.

Please amend the last paragraph beginning on page 7 as follows:

After heat treatment, the first intermediate is quenched at a high rate to form a second intermediate. In one embodiment, the cooling rate during this quench is within the range from about 20 to about 200°C/second. A high quench rate promotes small second phase precipitate particle size and high solute retention in the matrix of the creep resistant zirconium alloy. This is needed for resistance to nodular corrosion in a boiling water reactor. If the cooling rate was too slow, large second phase precipitate particles would form. If the cooling rate was too fast, very few second phase precipitates would form, and there would be poor uniform corrosion in a boiling water reactor environment.

Please amend the second full paragraph on page 8 as follows:

After cold working, the third intermediate is annealed at an elevated temperature to effect partial recrystallization. In one embodiment, the annealing is conducted [with] within the temperature range from about 580°C to about 640°C.

Please amend the fourth full paragraph on page 9 as follows:

The effect of temperature on the rate of hydrogen gas cracking was also determined at an initial stress intensity of $32 \text{ ksi}\sqrt{\text{in}}$. Hydrogen cracking in plate A was rapid at both 250°C and 325°C , Figures 2A and 3A. Tests on Plate A that were conducted at 250°C exhibited low cracking rates at the initial stress intensity of $32 \text{ ksi}\sqrt{\text{in}}$, but the rate of crack propagation at the highest stress [intensifies] intensities was very similar for both temperatures.

Please amend the first full paragraph on page 10 as follows:

The stress intensity of the 250°C Plate B sample was increased from $34 \text{ ksi}\sqrt{\text{in}}$ to $39 \text{ ksi}\sqrt{\text{in}}$ which led to another transient increase in the crack propagation rate to $1 \times 10^{-4} \text{ in/s}$ followed by a drop to a steady state rate of $5 \times 10^{-6} \text{ in/s}$. It is believed that the [behaviour] behavior of Plate B at 34 and $39 \text{ ksi}\sqrt{\text{in}}$ was consistent with transient growth of the crack tip plastic zone size under primary creep conditions. Once an equilibrium plastic zone size was achieved, steady state creep rates controlled the rate of crack advance. For this reason, Figure 3B shows the locus of steady state cracking rates in addition to the transient cracking [behaviour] behavior.

Please amend the second full paragraph on page 11 as follows:

The difference in [behaviour] behavior between cold-worked and partially recrystallized Plate B may be due to either their difference in creep strength or the lower applied stress intensity of the cold-worked sample. It is believed that both were factors. This result is significant because it indicated that no hydrogen gas fracture occurred at low stress [intensifies] intensities relative to the creep cracking threshold of the material.

Please amend the last full paragraph on page 11 as follows:

Plate A exhibited steady crack growth in air at 325°C at an initial rapid rate which dropped to a slower steady state rate of $1.5 \times 10^{-4} \text{ in/s}$ approximately 175 [s.] seconds

after load application. The crack propagation rate then accelerated to a rate of 10^{-2} in/s as the stress intensity increased because of crack extension. Specimen failure occurred. SEM fractography showed that fracture was by ductile microvoid nucleation and growth. Similar transient high rate cracking, slower steady state cracking, and tertiary cracking [behaviour] behavior has been observed in creep cracking of rotor steels. The failure of Plate A in air at 325°C is thus best described as creep cracking.

Please amend the first full paragraph on page 12 as follows:

Plate B exhibited an initial crack growth rate of 10^{-3} in/s in air at 325°C at the same 32 ksi√in stress intensity, Figures 5A and 6B. The crack propagation rate of Plate B dropped rapidly to 10^{-7} in/s immediately after loading, however[.], and further [Further] crack advance was minimal. After 5000 [s] seconds, the stress intensity of Plate B was increased to 38 ksi√in and the resulting crack advance is shown in Figure 5B. After loading to 38 ksi√in, the sample exhibited a transient high propagation rate followed by a slower steady state rate and then acceleration to failure at higher stress [intensifies] intensities. The minimum crack propagation rate of Plate B was 5×10^{-5} in/s[.] which occurred at a stress intensity of 45 ksi√in. SEM fractography showed that failure was also by ductile microvoid nucleation and growth.

Please amend the third full paragraph on page 12 as follows:

A comparison of 325°C air and hydrogen cracking of Plate A in Figures 2A and 2B and 5A and 5B showed that the rate of cracking of Plate A in hydrogen gas at 750 psig was much faster than the rate of creep cracking in air at [the] that stress intensity. The initial rate of cracking in both air and hydrogen were similar, but while air cracking followed a curve of decreasing crack rate, hydrogen cracking accelerated rapidly to a maximum value of 0.05 to 0.15 in/s. SEM fractography showed that the sample that was tested in air had a locally ductile micro dimpled fracture surface while the sample of Plate A that was tested in hydrogen had a perfectly brittle fracture surface.

Please amend the ABSTRACT as follows:

The present invention provides a creep resistant zirconium alloy comprising a coarse grained lath alpha microstructure. The microstructure can include small second phase precipitates. The small second phase precipitates can have a diameter less than 0.15 μ m. The microstructure can be partially recrystallized. [The microstructure is an acicular structure and can include a lath spacing within the range from about 0.5 to about 3.0 μ m.] The microstructure is an acicular structure and can include a lath spacing within the range from about 0.5 to about 3.0 μ m. The present invention provides a nuclear fuel cladding comprising an annular layer of the creep resistant zirconium alloy. The present invention also provides a method of manufacturing a creep resistant zirconium alloy comprising the steps of [beat] beta heat treating a zirconium alloy to form a first intermediate, fast quenching the first intermediate to form a second intermediate, cold working the second intermediate within the range from about 30% to about 40% to form a third intermediate, and annealing the third intermediate to effect partial recrystallization.

Amendments in the Claims:

In accordance with 37 C.F.R. § 1.121(c)(1), the following replacement claims show all of the changes made by the foregoing amendments relative to the previous versions of the claims. Material added is shown underlined, material deleted is shown in [brackets].

2. (Amended) The zirconium alloy as claimed in claim 1 wherein the microstructure comprises [includes small] second phase precipitates.

3. (Amended) The zirconium alloy as claimed in claim [1] 2 wherein the [small] second phase precipitates have a diameter less than about 0.15 μ m.

6. (Amended) The zirconium alloy as claimed in claim 1 wherein the microstructure has an acicular structure [which includes] comprising a lath spacing within the range from about 0.5 μ m to about 3.0 μ m.

7. (Amended) The zirconium alloy as claimed in claim 5 wherein the microstructure is an acicular structure and [includes] comprises a lath spacing within the range from about 0.5 μ m to about 3.0 μ m.